

The University of Chicago

THE HEATS OF DILUTION OF
AQUEOUS SOLUTIONS OF HYDRO-
CHLORIC ACID

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By

MIRIAM GERTRUDE BUCK

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INTRODUCTION

Precise values for activity coefficients are necessary for the complete understanding of electrolytes. In this laboratory, there is a program for the comparison of methods used for the calculation of activity coefficients such as the freezing point and electromotive force methods. Hydrochloric acid is an especially good electrolyte with which to make such comparisons since the electromotive force data for this acid are very precise and the activity coefficients calculated therefrom are probably better than those for any other solute. For the calculation of activity coefficients from the freezing point data, heats of dilution are required.

A number of workers have made measurements of heats of dilution of hydrochloric acid. Their methods, which involved the use of mercury thermometers, have not yielded sufficiently precise data for these calculations.

Berthelot,¹ as early as 1875, made a number of measurements of heats of dilution of hydrochloric acid. His dilutions were made at temperatures varying from 13° to 17° C. and he states that the results obtained are not of sufficient precision to warrant a temperature correction to make them comparable.

Steinwehr,² in 1903, made a few determinations of heats of dilution of hydrochloric acid at about 16° C. He diluted four solutions in the range of $m = 0.2212$ to $m = 4.243$ with large

¹Berthelot, Ann d. Chim., 5th Series, 4, 467 (1875).

²Steinwehr, Z. Physik. Chem., 38, 185 (1903).

amounts of water. His results agree poorly among themselves.

Muller³ made a series of dilutions of normal hydrochloric acid. His dilutions were made to three concentrations at three temperatures.

Richards and Rowe⁴ determined the heats of dilution of hydrochloric acid at two different temperatures (16° and 20° C.) as an indirect method for the determination of specific heats of dilute solutions. They diluted two solutions ($m = 5.5507$ and $m = 2.77535$) to concentrations ranging from 0.14 to 2.22 molal.

Wrewsky and Sawaritzsky⁵ measured heats of dilution of seven solutions ranging from 1.1 to 15.6 molal. These were all diluted to a molality of 0.27755 at 15° C. The same workers measured heats of solution of hydrochloric acid at four different temperatures. The results may be used to calculate heats of dilution, but the values would not be so precise as those obtained from their direct measurements.

Richards, Mair and Hall⁶ repeated the work of Richards and Rowe and extended the dilutions to 0.07 molal.

Combining the measurements of the above investigators with some heat capacity data, Rossini⁷ calculated and plotted values for the apparent molal and partial molal heat contents of hydrochloric acid at 18° and 25° C. Elsewhere⁸ he calls attention to the fact that the available data for hydrochloric acid are not

³Muller, Bull. Soc. Chim., 13, 1053 (1913).

⁴Richards and Rowe, J. Am. Chem. Soc., 42, 1621 (1920).

⁵Wrewsky and Sawaritzsky, Z. Physik. Chem., 112, 90 (1924).

⁶Richards, Mair and Hall, J. Am. Chem. Soc., 51, 727 (1929).

⁷(a) Rossini, Bur. Standards J. Research, 6, 727 (1929);
(b) Ibid., 9, 679 (1932).

⁸Ibid., 7, 47 (1931).

consistent among themselves.

The present research was undertaken to obtain heat of dilution data of sufficient precision for the calculation of partial molal heat contents. This precision is more readily obtained by the dilution of a comparatively large volume of solution with a small volume of water, the reverse of the process used in the investigations cited. The results obtained are interesting as a check on heats of dilution calculated from electromotive force data since direct measurements are much more precise.

APPARATUS

The apparatus was essentially the same as that used by Groenier⁹ and Machin¹⁰ and was similar to that described by Young and Vogel.¹¹ The Dewar flask used as a calorimeter was made of Pyrex glass. The dilution vessel used in some preliminary experiments was a silver capsule similar to the one used by Groenier and by Machin except that gold solder was used in its construction.¹² Since deposits of silver chloride formed on this capsule when it was immersed in hydrochloric acid solutions, conductivity measurements were repeatedly made upon the solutions before and after immersion of the vessel to determine whether corrosion would continue indefinitely. These tests showed that the actual concentration changes were so small that errors arising therefrom would probably not affect the results within the accuracy of the apparatus. However, it seemed inadvisable to risk even the slight pos-

⁹Groenier, Ph. D. Dissertation, University of Chicago (1931).

¹⁰Machin, Ph.D. Dissertation, University of Chicago (1932).

¹¹Young and Vogel, J. Am. Chem. Soc., **54**, 3030 (1932).

¹²This solder, according to the manufacturers, Thomas J. Dee and Company, contained 530 parts in 1000 of gold, the remainder being silver, copper and another element not specified.

sibility of a larger error from this source and so a tantalum vessel which would be resistant to the acid solutions was designed.

This vessel (fabricated by the Fansteel Products Company) had a capacity of about seventy-five cubic centimeters. It is shown in diagrammatic form in Figure 1. The main cylindrical portion, A, and the lower truncated cone, B, were spun in one piece. The upper section, C, was welded to the cylinder, A. Both the upper and the lower openings were fitted with ground valves, D and E. The lower valve, E, was welded to a tantalum rod, F, which extended through one of the chimneys on the top of the calorimeter. The upper valve, D, was welded to a tantalum tube, G, seven centimeters long, made to fit the rod, F, very closely. When in use, the very small space between the rod and the tube was nearly filled with vaseline. This reduced the friction of opening, permitted only a very small amount of solution to be held in the space between the rod and the tube and prevented evaporation of water from the can into the solution. The maximum amount of liquid which could have been held in this space if no vaseline were present was 0.0686 cubic centimeters. Since the volume of solution used was approximately 790 cubic centimeters and that of the water about 73 cubic centimeters, this would introduce an error of less than 0.01 per cent if the space were filled with the original solution, and an error of less than 0.1 per cent if it were filled with the diluting water. Since the space was practically filled with vaseline, the actual error from this source was obviously negligible.

A small collar, H, was welded to the rod so that it would be two millimeters below the upper valve when it was seated. A pull on the rod, F, opened the lower valve and immediately afterward the upper valve. The upper opening was larger than the lower

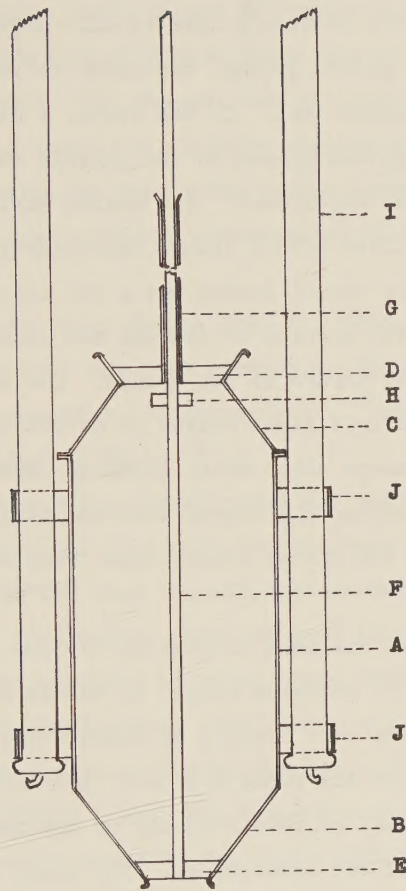


FIGURE 1.

so that the rod and valves could be completely removed from the capsule for cleaning. After each valve was closed, the exposed surfaces of the valve and valve seat were covered with molten vaseline, spread on with a camel's hair brush. This, in conjunction with the ground joints, was shown by repeated tests to provide a non-leaking seal. In the tests, a dilute solution of ferric chloride was placed in the capsule which was then sealed as in a regular experiment. The sealed capsule was immersed in a tall beaker filled with a dilute thiocyanate solution. If the contents of the vessel leaked out a red color developed at the leak. The outer surface of the can was washed in a stream of distilled water before it was opened. The contents of the can were collected in a clean beaker to detect the presence of any ferric thiocyanate which would indicate leakage into the can. In no case was leakage discovered when the seals were covered with vaseline, but the ground joints alone were not proof against leakage.

The can was held in position by two Pyrex rods, I, which were inserted in tantalum rings, J, welded to the can. The lower ends of the rods were flanged to support the lower rings. A small Pyrex knob was fused onto the flat end of each rod so that the capsule could be held securely by platinum wires attached to these knobs and the lower rings. The glass rods extended up through two brass chimneys on the top of the calorimeter and were prevented from slipping by pieces of tightly fitting rubber tubing wired to the rods and chimneys.

The stirrer which was made of tantalum was cemented into glass tubing to reduce the conduction of heat into or out of the calorimeter. It was rotated through gears by a small synchronous motor at 450 revolutions per minute.

The thermel was a twenty-four junction element made of copper and constantan wires, numbers 32 and 24 Brown and Sharpe gauge, respectively. It was repaired twice during these investigations, the second time, small pieces of pongee silk were used to insure perfect insulation at points where the original insulation appeared to be worn. The thermel was calibrated in the neighborhood of 25° C. against a platinum resistance thermometer which had been calibrated by the United States Bureau of Standards. A thermel reading of one microvolt corresponded to 0.001056 degree at 25° C.

A copper shield which dipped into the water provided a nearly uniform temperature for that portion of the thermel which extended above the thermostat and calorimeter. This was in accordance with the suggestion of White.¹³

A constant temperature environment was provided for one end of the thermel by means of a pear shaped Dewar flask immersed in the thermostat. At the time the calorimeter was placed in the thermostat and again just before readings were taken, the water in the Dewar flask was replaced by water drawn from the thermostat. To insure temperature equilibrium, about three liters of the thermostat water were siphoned through the Dewar flask which was then closed with a divided cork. The temperature of the water in the Dewar flask was not subject to the short period fluctuations in the temperature of the thermostat which were about 0.001 degree. The mean deviation of the thermel readings from the straight line representing the calorimeter temperature just prior to a dilution was 0.0132 microvolt, corresponding to a galvanometer deflection of only 0.119 millimeter which was the precision of reading.

The thermostat, a tank 76 x 76 x 61 centimeters was

¹³White, J. Am. Chem. Soc., 36, 2292 (1914).

covered with a celotex shield about 72 centimeters in height, three sides of which were removable. This cover diminished the effect of sudden temperature changes in the surroundings. The thermostat temperature was maintained by a large mercury in glass regulator operating a relay which controlled a 500 watt heating bulb. Originally a tungsten wire was sealed into the glass of the regulator to make contact with the mercury in the side arm. The resistance of this wire became great enough at times to affect the regulation materially. To eliminate this difficulty, the tungsten wire was replaced by a piece to the ends of which had been welded pieces of platinum wire. At the time the wire was changed, the capillary was changed to one of larger bore, namely 2.1 millimeters, since it was suspected that some of the difficulty in regulation may have been due to oxidation of the mercury surface caused by sparking. A portion of the mercury was withdrawn from the capillary daily to insure a clean contact surface. The temperature was thus kept constant to ± 0.001 degree for the period of an hour or more necessary for the measurements to be made. The temperature did not vary by more than one or two hundredths of a degree from day to day. Two auxiliary heaters, one, a second 500 watt bulb, and the other, a metal encased electric heater were used to increase the temperature of the bath rapidly. Three cooling coils of varying sizes were used to assist in the regulation of the temperature.

The temperature of the bath was read from two thermometers suspended in the thermostat. To avoid errors due to parallax, they were read with the aid of a telescope. One thermometer, graduated in tenths of degrees had been calibrated by comparison with a Bureau of Standards certified thermometer, the other, a Beckmann thermometer, was used only to check the constancy of the

temperature.

The heater for the calorimeter was the one described by Groenier¹⁴ and used later by Machin.¹⁵ During the course of these experiments, a short circuit occurred in the heater. When it was dismantled, this short circuit was found to be between one of the leads and the case. Hence, it was possible to use the same heating coil again. To reinforce them, the leads were passed through holes in the mica strips in such a way that a strain upon the leads could not pull the soldered connections. The resistance of the heater was changed slightly due to the repairs. While the heater was disassembled, a platinum wire was wound tightly around the end of the platinum-iridium tube to provide a means of connecting the heater with the ground. A No. 26 copper wire was soldered to the platinum wire and was brought out through the bakelite top.

The Type HS galvanometer and the White Double Potentiometer used throughout the experiments were made by Leeds and Northrup.

To provide critical damping for the galvanometer, it was necessary to change the resistance of the copper coil which shunted the galvanometer from approximately forty-two to twenty ohms. The new coil was made of No. 30 copper wire wound non-inductively on a wooden spool. The ends of the wire were soldered to heavy copper leads which passed through small holes drilled through the core. Any strain was thus put upon the leads instead of upon the soldered joints. With the galvanometer critically damped the thermel produced a galvanometer deflection of about nine millimeters per microvolt on a scale at a distance of four meters. A new check coil made in the same manner as the galvanometer shunt coil was substituted for the one previously used.

¹⁴Loc. cit.

¹⁵Loc. cit.

All the leads connecting the instruments were of copper. Both the galvanometer and thermel leads were crossed at intervals in order to cancel stray electromotive forces which arose from fluctuations in the magnetic field in the laboratory.

The heater circuit used by Groenier¹⁶ and by Machin¹⁷ was revised. To steady the current from a fifty volt battery, the old circuit required an auxiliary resistance equal to that of a network which consisted of the heater and a 0.1 ohm standard resistance in parallel with a 1.0 ohm standard resistance and a 10,000 ohm resistance. In the new arrangement, the auxiliary resistance was approximately equal to the heater alone. The revised circuit made it possible to measure the current both before and after the heating period to check its constancy and also made it possible to determine the resistance of the auxiliary resistance as well as that of the heater while it was in use. The current was computed from the fall of potential over the standard 0.1 ohm resistance connected in series with either the heater or the auxiliary resistance. The heating circuit is shown in Figure 2.

The heating period was controlled by a combination manually and clock operated system similar to that described by Groenier.¹⁸ The revised system included a toggle switch, a single pole-single throw switch and a double pole-double throw switch shown in Figure 2.

In the experiments with the more concentrated solutions in which the heating effect due to dilution was large, it was necessary to allow the calorimeter to cool before current was passed through the heater. The use of an ice pack made of unbleached drilling to fit snugly around the calorimeter reduced

¹⁶Loc. cit.

¹⁷Loc. cit.

¹⁸Loc. cit.

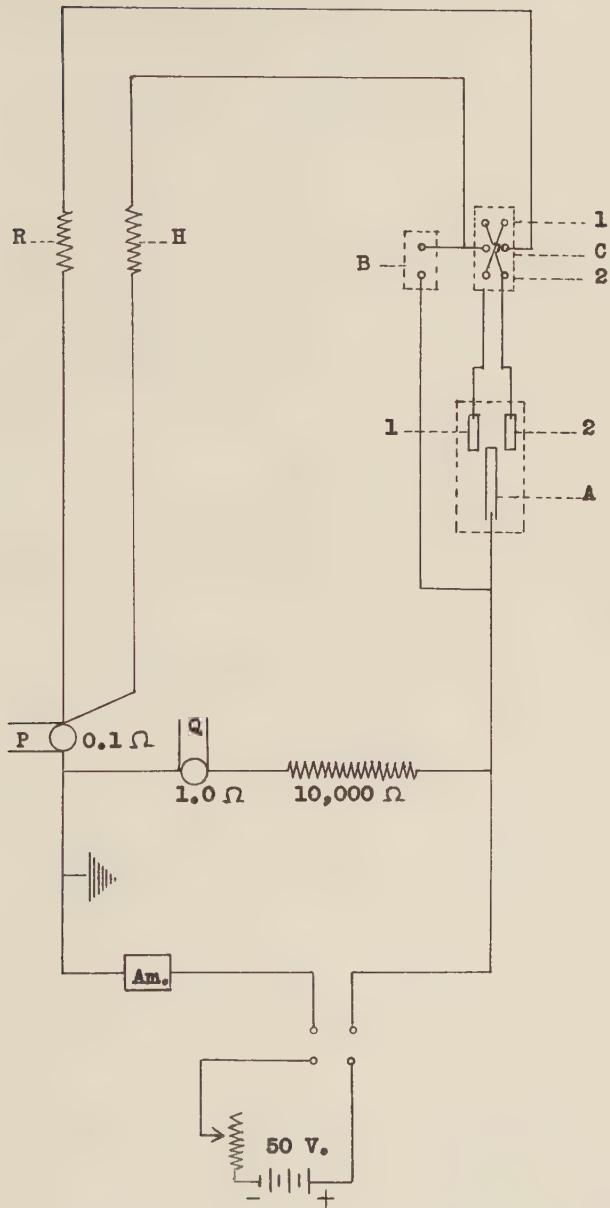


FIGURE 2.

KEY TO FIGURE 2

H. Heater

R. Auxiliary Resistance

B. Single pole-single throw switch

C. Double pole-double throw switch

A. Wall switch

 1. Upper Contact

 2. Lower Contact

P. Leads to P dials of potentiometer

Q. Leads to Q dials of potentiometer.

the cooling time by four or five hours. The two auxiliary heaters were used to diminish the cooling of the thermostat while the ice pack was in use and to restore the original temperature of the thermostat after the removal of the ice pack. The original temperature of the bath was restored in approximately three-quarters of an hour.

Two pear shaped burettes fitted with ground glass stoppers and tip caps were used for the determination of the weights of the solutions and the distilling water. Care was exercised to prevent evaporation of the solution and water and all weights were corrected to weight in vacuo.

MATERIALS

The solutions were made from Baker and Adamson's C.P. Reagent Quality Hydrochloric Acid. For most of the solutions, the C.P. acid was distilled before use. A one liter Pyrex all-glass still was made according to the specifications of Foulk and Hollingsworth¹⁹ with the exception that no provision was made to maintain constant pressure. Consequently, it was impossible to use the constant boiling acid as a standard in making the solutions. The distillates were collected in a Pyrex Erlenmeyer flask. A special adapter was made to fit the flask loosely to reduce evaporation of the distillate.

The C.P. acid was diluted with distilled water to a solution having a specific gravity of about 1.10. About the first third of the solution was distilled and collected. The remaining solution except for the last 50-60 cubic centimeters was distilled and collected for use. The distillate was transferred to a three liter Pyrex flask. This solution was used for all but four of the

¹⁹Foulk and Hollingsworth, J. Am. Chem. Soc., 45, 1220 (1923).

solutions to be used for dilution experiments. The 2.5612 m. solution was made from first distillates. The two most concentrated solutions ($m = 5.4019$ and $m = 4.0786$) were made directly from the C.P. acid. The most dilute solution ($m = 0.15963$) was made by weight dilution of the 4.0786 m. acid. The solutions with the exception of this most dilute solution were analyzed by the silver chloride residue method. The weight dilution value for the concentration of this solution was used in the calculations. When time permitted the hydrochloric acid distillates were analyzed by the silver chloride residue method and the final solutions made by weight dilution. The concentration values so obtained checked the silver chloride residue values closely (0.06% - 0.11%).

The method of analysis was a modification of Richard's method.²⁰ The modifications used were the same as those used by Hartsuch²¹ except that distilled water was substituted for conductivity water.

The solutions were stored in large Pyrex flasks stoppered with corks which had been treated with hot paraffin. Paper caps were used to protect the flasks from dust. The solutions were transferred to the weight burettes by means of a siphon. The mouths of the flasks were stoppered with cotton during this process to reduce evaporation.

EXPERIMENTAL PROCEDURE

The solution to be used was weighed in the large weight burette and the water in the smaller one. If the temperature of

²⁰(a) Richards and Willard, Carnegie Inst. Pub., No. 125, 26 (1910); (b) Richards and Wells, J. Am. Chem. Soc., 29, 487, 515 (1907); Carnegie Inst. Pub., No. 28, 25 (1905); J. Am. Chem. Soc., 32, 28 (1910); (c) Richards and Staehler, J. Am. Chem. Soc., 29, 632 (1907); Carnegie Inst. Pub., No. 69, 17 (1907).

²¹Hartsuch, Ph. D. Dissertation, University of Chicago (1935).

the room was higher than that of the thermostat, the filled and weighed burettes were suspended in the thermostat for an hour or more to cool. After the solution had been transferred to the calorimeter and the water to the dilution vessel, the latter was sealed, the calorimeter parts were assembled as rapidly as possible to reduce temperature changes and loss by evaporation and the assembly was placed in position in the thermostat.

The thermel was inserted, the stirrer started and the small Dewar flask siphoned as described previously. The thermel reading was then observed. Usually when the temperature of the calorimeter was below that of the thermostat by as much as fifty or more microvolts (approximately 0.05°C.), current was passed through the calorimeter heater until the temperature was one to thirty microvolts above that of the thermostat. Several hours were allowed for the calorimeter to reach equilibrium with the thermostat.

Whenever the temperature of the calorimeter was varying, the temperature of the dilution vessel and its contents lagged behind that of its surroundings. Therefore, it was necessary to insure that a steady state had been reached before a dilution was made. Landwehr²² has shown that the apparent heat of opening of dilution vessels observed in the determination of heats of dilution of dilute solutions was due to the fact that a state of true equilibrium had not been reached. A dilution was not made until the temperature change between the calorimeter and the reference Dewar flask was no greater than 0.02-0.03 microvolt per minute for a period of an hour or more.

During at least the last half hour and usually during the

²²Landwehr, Master's Dissertation, University of Chicago (1934).

last hour of this interval, current from the battery was passed through R, the auxiliary resistance, Figure 2. Switch A, which was controlled by the toggle-clock combination (not shown in the Figure) was in position 1 during this period.

The temperature of the thermostat was recorded and the sensitivity of the thermel determined. Thermel readings were then recorded for about twelve minutes. The dilution vessel was opened on the half minute and the thermel readings continued without interruption for about twelve minutes more.

The current was next passed through the heater for exactly three minutes after which temperature readings were again recorded for ten to twelve minutes. The purpose of the heating period was, of course, to obtain the heat capacity of the calorimeter and contents. A second heating period of three minutes followed by measurements of the temperature drift was used as a check. If the heat capacity values did not check within about 0.1 per cent, a third and possibly a fourth heating period was used. The average deviation from the mean in these cases was then not greater than 0.12 per cent. In one experiment, the additional heat capacity measurements were not made before the solution was discarded and the whole determination was therefore rejected. Extrapolations to obtain the exact temperature changes were made in the manner described by Young and Vogel.²³

To start the heating period, the toggle switch was closed and the exact second noted when the clock caused switch A to drop from position 1 to 2. The toggle switch was then restored to its normal position, switch B closed, creating a by-pass for the current, switch C was opened, A raised to position 1, and C moved

²³Loc. cit.

to position 2. Part of the current passed through switch B and part of it through A-1 and C-2 for the greater part of the heating period. The operation of the switches required less than five seconds. Two to five seconds before the end of the heating period, switch B was opened and on the exact second, the toggle-clock system lowered switch A from position 1 to 2 thus breaking the circuit through the heater and sending the current through the auxiliary resistance. Switch C was opened, A raised to 1, and C moved to position 2. This restored the original conditions in preparation for a second heating period.

At the middle of each heating period, the current was measured on the P dials of the potentiometer. After the completion of each dilution experiment, the temperature of the thermostat was again recorded. The current through the heater and the drop in potential across the standard 1.0 ohm resistance were then measured to determine the resistance of the heater by use of the formula:

$$R_h = (Q/P)1000.1 - 0.3,$$

where R_h is the resistance of the heater in ohms, Q, the reading on the Q dials in microvolts, and P, the reading on the P dials in microvolts. The resistance of the heater did not vary more than 0.016 per cent during the course of the experiments.

The resistance of the leads was measured a number of times throughout the course of the experiments and was found to be practically constant with a value of 0.2 ohm.

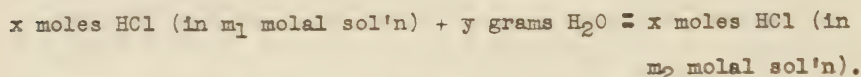
CALCULATIONS AND RESULTS

The energy input for each heating period was derived from the familiar equation,

$$E = \frac{I^2 R t}{4.185},$$

where I is the current in amperes at the middle of the heating

period; R , the resistance of the heater in ohms; t , the time in seconds (180 seconds in these experiments); and 4.185, the number of joules per 15° calorie. This value of E divided by the number of microvolts change during the heating period yields the heat capacity of the calorimeter and contents in calories per microvolt. The number of microvolts change caused by the dilution multiplied by the mean of the heat capacity determinations yields ΔH for the isothermal process:



This value divided by x is $\Delta \phi H$ in calories per mole. The derivative, $d\phi H/d\sqrt{m}$, has been designated as the slope, S ,²⁴ the value of the ordinate of any point on the curve in Figure 3. The value $\Delta \phi H$ divided by $\Delta\sqrt{m}$, i.e., $\sqrt{m_2} - \sqrt{m_1}$, is the average value of S between $\sqrt{m_1}$ and $\sqrt{m_2}$. This function is designated as $\bar{F}_t^\circ$ in Table I, column 11.²⁵

The temperature of the calorimeter at the instant of dilution was determined from the temperature of the thermostat, the thermel reading and the temperature change necessary to cause one microvolt change in the electromotive force of the thermel. The value of $\bar{F}_t^\circ$ was corrected to 25° C. in the following manner. The apparent molal heat capacity, ϕ_c , is the derivative of the apparent molal heat content with respect to temperature. Therefore, $\phi_c = d\phi H/dt$. If then, ϕ_c is plotted against $\sqrt{m}$, the slope of the curve is the temperature coefficient of S or $\bar{F}$. This slope multiplied by the difference between the temperature of the dilution and 25° C. gives the correction to be added to $\bar{F}_t^\circ$. At concentrations greater than $\sqrt{m} = 1.56$, the value of 7.2 given

²⁴Young and Vogel, loc. cit.

²⁵For a complete derivation of this expression with an appropriate example, see Machin, loc. cit.

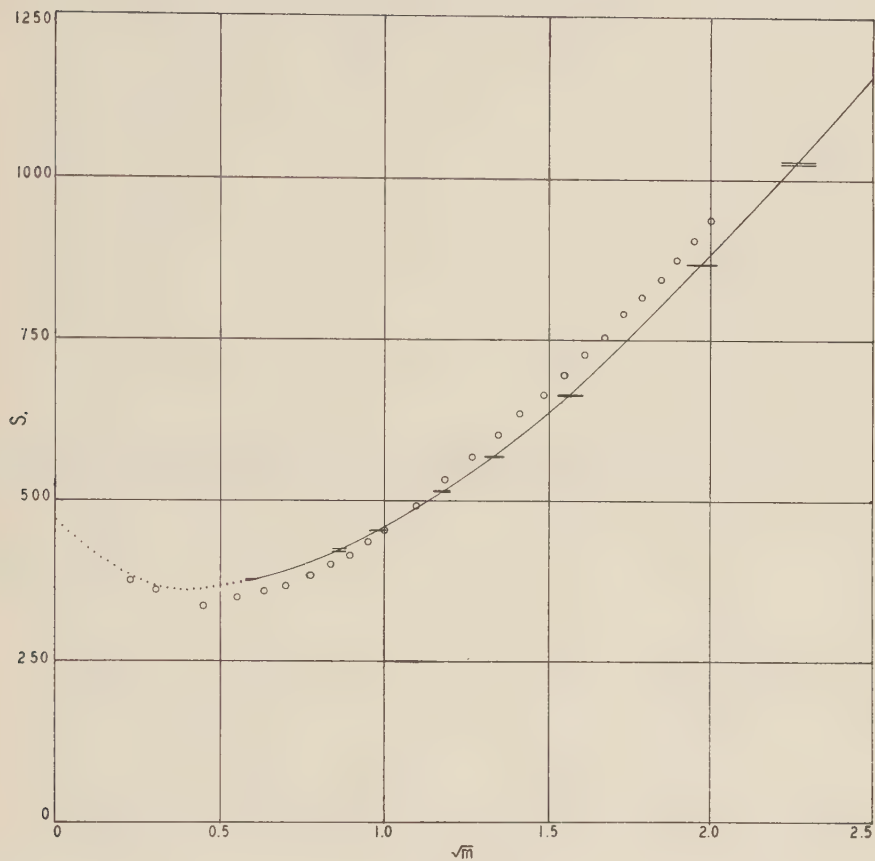


FIGURE 3.

Chords represent calorimetric measurements of heats of dilution.

Circles calculated from Harned and Ehlers' e.m.f. data.

TABLE I

No.	m_1	$\sqrt{m_1}$	$\sqrt{m_2}$	$t_0 \pm 0.01^\circ$	Δt in $\mu v.$	$E_{\text{in Cal.}} \mu v^{-1}$	$E_{\text{(Average)}} \mu v^{-1}$	ΔH	$\Delta \phi H$	F_{t_0}	F_{250}
1.	0.156300	0.395372	0.3819232	24.96	0.80	.9379 .9414 .9450 .9441	.9421	- 0.75368	- 6.02776	342.2	342.2
2.	0.3670100	0.6058135	0.5792944	24.97	3.08	.9326 .9316	.9321	- 2.8709	- 9.99852	377.0	377.2
3.	0.3670100	0.6058135	0.5792336	24.95	3.07	.9331 .9349 .9365 .9342	.9347	- 2.8695	- 9.97284	375.2	375.4
4.	0.7743300	0.8799602	0.8410397	24.97	10.72	.9168 .9165	.9167	- 9.8270	-16.40783	421.6	421.7
5.	0.7743300	0.8799602	0.8408148	24.98	10.90	.9109 .9091	.9100	- 9.9190	-16.69082	426.4	426.5
6.	1.0004500	1.0002250	0.9555593	24.97	17.18	.9092 .9089 .9080	.9087	-15.611	-20.24896	453.3	453.5
7.	1.0004500	1.0002250	0.9559302	24.95	16.99	.9100 .9106	.9103	-15.466	-20.05593	452.8	453.0
8.	1.4419700	1.2008206	1.1465259	24.95	34.18	.8935 .8937	.8936	-30.543	-27.85670	513.1	513.3
9.	1.4419700	1.2008206	1.1463508	24.96	34.34	.8922 .8948					

TABLE I--CONTINUED

No.	m_1	$\sqrt{m_1}$	$\sqrt{m_2}$	t^0 $\pm 0.01^0$	Δt in μv .	E μv^{-1} Cal., 150	E μv^{-1} (Average)	ΔH	$\Delta \phi E$	$\overline{P}_{t^0}$	$\overline{P}_{250}$
9.						.8924	.8931	-30.669	-28.04309	514.8	515.1
10.	1.858600	1.3633048	1.3011429	24.95	56.09	.8759 .8751	.8755	-49.107	-35.20640	569.1	569.4
11.	1.858600	1.3633048	1.3013939	24.95	56.06	.8813 .8819	.8816	-49.422	-35.19502	568.5	568.8
12.	2.561200	1.6003750	1.5270772	24.96	108.25	.8512 .8522 .8515	.8516	-92.186	-48.7115	664.6	664.9
13.	2.561200	1.6003750	1.5261200	24.96	109.60	.8435 .8453 .8433 .8429	.8438	-92.475	-49.3967	664.6	664.9
14.	2.561200	1.6003750	1.5270355	24.97	108.54	.8540 .8538	.8539	-92.688	-49.6297	663.1	663.3
15.	4.078600	2.0195544	1.9245847	25.00	296.07	.8265 .8275	.8270	-244.85	-82.4477	868.1	868.1
16.	4.078600	2.0195544	1.9238092	24.99	298.27	.8203 .8276 .8227 .8226	.8223	-245.27	-83.0018	866.9	870.0
17.	5.401900	2.3241988	2.2135046	24.96	551.72	.7862 .7863	.78625	-433.790	-113.5077	1025.4	1025.7
18.	5.401900	2.3241988	2.2103328	24.95	565.24	.7798 .7797	.77975	-440.746	-117.1614	1028.9	1029.3

by Rossini²⁶ was used for this slope. Below that concentration, values obtained from the curve of Gucker and Schminke²⁷ were used. The corrections in all cases were far less than the experimental error but were applied, nevertheless. The values of $\bar{F}_{250}$ are given in Table I, column 12 and are plotted as chords between $\sqrt{m_1}$ and $\sqrt{m_2}$ in Figure 3.

The curve is drawn according to the method described by Young and Vogel.²⁸ A more exact curve could be drawn by their method for the "Final Construction of Differential Curve." Since the chords in this work are all short, the corrections would be within the limits of error in reading the graph. The curve is dotted between $\sqrt{m} = 0.6$ and infinite dilution. One value was obtained in this region. The heat effect in this case was so small (0.0008°) that the precision of reading the graph for the dilution experiment was such as to introduce a possible error of 5 per cent. This would be sufficient to account for the difference in the position of the dotted line and the uncertain value obtained by experiments.

DISCUSSION OF RESULTS

The results obtained indicate that distillation of the hydrochloric acid was not necessary to insure its purity.

Only 0.1 per cent precision is claimed for the values of the heat capacity of the calorimeter and contents though in most cases this precision was exceeded.

The current during a heating period was assumed to be constant and equal to the current at the middle of the period, the

²⁶Rossini, Bur. Standards J. Research, 9, 679 (1932).

²⁷Gucker and Schminke, J. Am. Chem. Soc., 54, 1358 (1932).

²⁸Loc. cit.

time when it was measured. It could not have varied to any perceptible extent since the difference between the currents of two consecutive heating periods which were at least seventeen minutes apart never varied by more than 0.07 per cent and the average difference was only 0.017 per cent.

Since the apparatus used is not sufficiently precise for the determination of heats of dilution of dilute solutions, relative partial molal heat contents referred to infinite dilution as a standard state cannot be given. It is, however, a comparatively simple matter to obtain values for the relative partial molal heat contents referred to $m = 1.0$ as an arbitrary reference state. This was done by mechanical integration of the "S" plot and use of the equation,

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0 = \phi_H - \phi_H^0 + \frac{\sqrt{m}}{2} S,$$

which becomes

$$\bar{L}_2 - \bar{L}_{2(1m.)} = \bar{H}_2 - \bar{H}_{2(1m.)} = \phi_H - \phi_{H(1m.)} + \frac{\sqrt{m}}{2} S - \left[\frac{\sqrt{m}}{2} S \right]_{(1m.)}$$

The values of $\bar{L}_2 - \bar{L}_{2(1m.)}$ are shown by the solid curve of Figure 4. Corresponding values obtained from the values of Harned and Ehlers²⁹ calculated from electromotive force data are shown as the dotted curve of Figure 4. The values obtained from Rossini's calculations of $\bar{H}_2 - \bar{H}_2^0$ ³⁰ are shown as circles. These values are in almost perfect agreement with those of the author above the concentration $\sqrt{m} = 0.6$. Rossini based his calculations upon an estimate of the best data available. Inasmuch as he realized that the data were rather discordant, the close agreement is accidental. The relative partial molal heat contents calculated

²⁹Harned and Ehlers, J. Am. Chem. Soc., **55**, 2179 (1933).

³⁰Cf. reference cited in footnote 7(b).

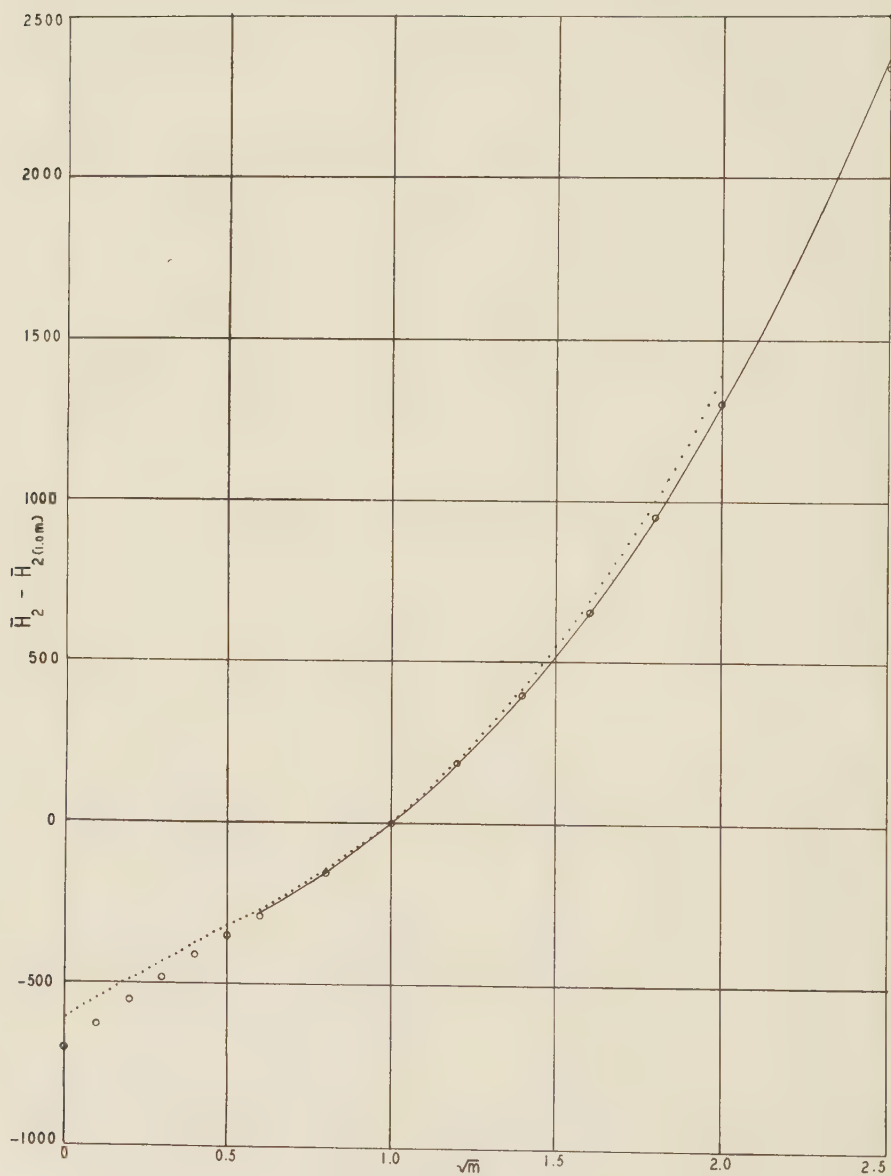


FIGURE 4.

from electromotive force and heat of dilution data agree as well as could be expected. Nevertheless, the divergence shows the inadequacy of electromotive force data for the calculation of these thermodynamic quantities.

Another method of comparison with electromotive force data is to convert the values of the relative molal heat contents so obtained to "slope" values. Since $\Delta \phi H = \frac{1}{m} \int L_2 \, dm$, S , the derivative of $\Delta \phi H$ with respect to $\sqrt{m}$ is equal to

$$\frac{d}{d\sqrt{m}} \left[\frac{1}{m} \int L_2 \, dm \right]$$

which, upon differentiation becomes

$$\frac{2}{\sqrt{m}} \left[L_2 - \frac{1}{m} \int L_2 \, dm \right].$$

The first term of this quantity is obtained directly from values of L_2 found from the electromotive force data, the second term is easily obtained after mechanical integration of a plot of L_2 versus m . Results so obtained from the L_2 values of Harned and Ehlers are shown as circles in Figure 3.

It is interesting to compare the slope curve for hydrochloric acid with that for sodium chloride.³¹ The value for S for sodium chloride is negative for solutions more concentrated than 0.16 molal and changes sign in the more dilute solutions, that for hydrochloric acid is positive throughout the entire range. It is impossible to predict either the "slope" or relative molal heat contents of one electrolyte from those of another. Calorimetric measurements are necessary to obtain values of the function, S , to be used with freezing point data for the accurate evaluation of the activity coefficients of strong electrolytes.

³¹Young and Vogel, loc. cit.

SUMMARY

Existing heat of dilution data for hydrochloric acid have been examined and evaluated. Additional data have been obtained at 25° C. in the range of 0.16 m. to 5.40 m.

A comparison has been made of the relative molal heat contents obtained from electromotive force and calorimetric data. The agreement is satisfactory but shows the inadequacy of electromotive force data for the calculation of these thermodynamic quantities. Calorimetric measurements are necessary for the determination of precise thermo-chemical properties of solutions.

The author wishes to express her sincere appreciation to Dr. T. F. Young for his interest and many helpful suggestions without which this research could not have been completed.

